

**(12) PATENT**  
**(19) AUSTRALIAN PATENT OFFICE**

**(11) Application No. AU 199859873 B2**  
**(10) Patent No. 719308**

**(54) Title**  
**Photoactivatable nitrogen-containing bases based on alpha-amino ketones**

**(51)<sup>7</sup> International Patent Classification(s)**  
**C07D 487/04 C07D 519/00**

**(21) Application No: 199859873** **(22) Application Date: 1998.01.09**

**(87) WIPO No: WO98/32756**

**(30) Priority Data**

<b>(31) Number</b>	<b>(32) Date</b>	<b>(33) Country</b>
<b>133/97</b>	<b>1997.01.22</b>	<b>CH</b>

**(43) Publication Date : 1998.08.18**

**(43) Publication Journal Date : 1998.10.01**

**(44) Accepted Journal Date : 2000.05.04**

**(71) Applicant(s)**  
**Ciba Specialty Chemicals Holding Inc.**

**(72) Inventor(s)**  
**Veronique Hall-Goulle; Sean Colm Turner**

**(74) Agent/Attorney**  
**DAVIES COLLISON CAVE, GPO Box 3876, SYDNEY NSW 2001**

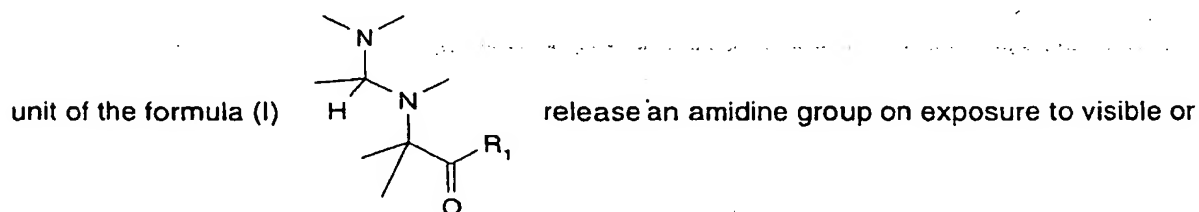
Photoactivatable nitrogen-containing bases based on  $\alpha$ -amino ketones

The invention relates to  $\alpha$ -amino ketones which can be converted photochemically into amidine derivatives, to a process for their preparation and to a process for the photochemical preparation of the amidine derivatives. Further subjects of the invention are base-polymerizable or crosslinkable compositions comprising these  $\alpha$ -amino ketones, a method of implementing photochemically induced, base-catalysed reactions, and the use of the  $\alpha$ -amino ketones as photoinitiators for base-catalysed reactions.

The photolytic cleavage of specific  $\alpha$ -amino ketones into free radicals and the photopolymerization of olefinically unsaturated monomers or oligomers which this initiates have long been known and are described, for example, in US 5077402.

In addition to free-radically polymerizable oligomers or monomers, base-catalysable systems have been disclosed in particular for photolithographic processes. These systems require a photoinitiator which on exposure to light releases a base. D. R. MacKean et al., Polym. Mater. Sci. Eng. (1992), 66, 237-238 report, for example, on the photostructuring of polyimide using specific carbamates as photoinitiators.

It has now surprisingly been found that certain  $\alpha$ -amino ketones which comprise a structural



UV light. This amidine group is sufficiently basic to initiate a large number of base-catalysable reactions, especially polymerization reactions. The compounds are of high sensitivity and through the choice of the substituent  $R_1$  the absorption spectrum can be varied within a wide range.

The compounds make it possible to prepare so-called one-pot systems with base-catalysable oligomers or monomers having an extremely long storage life. A polymerization reaction, for example, is initiated only after exposure to light. The systems can be formulated

- 3 -

$R_2$  and  $R_3$  independently of one another are hydrogen,  $C_1$ - $C_{18}$ alkyl,  $C_3$ - $C_{18}$ alkenyl,  $C_3$ - $C_{18}$ alkynyl or phenyl and, if  $R_2$  is hydrogen or  $C_1$ - $C_{18}$ alkyl,  $R_3$  is additionally a group  $-CO-R_{14}$  in which  $R_{14}$  is  $C_1$ - $C_{18}$ alkyl or phenyl; or  $R_1$  and  $R_3$ , together with the carbonyl group and the C atom to which  $R_3$  is attached, form a benzocyclopentanone radical;

$R_5$  is  $C_1$ - $C_{18}$ alkyl or  $NR_{15}R_{16}$ ;

$R_4$ ,  $R_6$ ,  $R_7$ ,  $R_{15}$  and  $R_{16}$  independently of one another are hydrogen or  $C_1$ - $C_{18}$ alkyl; or

$R_4$  and  $R_6$  together form a  $C_2$ - $C_{12}$ alkylene bridge or

$R_5$  and  $R_7$  together, independently of  $R_4$  and  $R_6$ , form a  $C_2$ - $C_{12}$ alkylene bridge or, if  $R_5$  is  $NR_{15}R_{16}$ ,  $R_{16}$  and  $R_7$  together form a  $C_2$ - $C_{12}$ alkylene bridge.

Alkyl in the various radicals having up to 18 carbon atoms is a branched or unbranched radical such as methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl. Preference is given to alkyl having 1 to 12, especially 1 to 6 carbon atoms.

Alkenyl having 3 to 18 carbon atoms is a branched or unbranched radical such as propenyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, iso-dodecenyl, oleyl, n-2-octadecenyl or n-4-octadecenyl. Preference is given to alkenyl having 3 to 12, especially 3 to 6 carbon atoms.

Alkynyl having 3 to 18 carbon atoms is a branched or unbranched radical such as propynyl ( $-\text{CH}_2-\text{C}\equiv\text{CH}$ ), 2-butylnyl, 3-butylnyl, n-2-octynyl, or n-2-octadecynyl. Preference is given to alkynyl having 3 to 12, especially 3 to 6 carbon atoms..

The  $C_2$ - $C_{12}$ alkylene bridge is ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene or dodecylene.

$R_1$  is preferably an aromatic radical which is unsubstituted or substituted one or more times by  $C_1$ - $C_{18}$ alkyl,  $C_3$ - $C_{18}$ alkenyl,  $C_3$ - $C_{18}$ alkynyl,  $C_1$ - $C_{18}$ haloalkyl,  $\text{NO}_2$ ,  $\text{NR}_8\text{R}_9$ ,  $\text{N}_3$ ,  $\text{OH}$ ,  $\text{CN}$ ,  $\text{OR}_{10}$ ,  $\text{SR}_{10}$ ,  $\text{C}(\text{O})\text{R}_{11}$ ,  $\text{C}(\text{O})\text{OR}_{12}$  or halogen and is selected from the group consisting of phenyl,

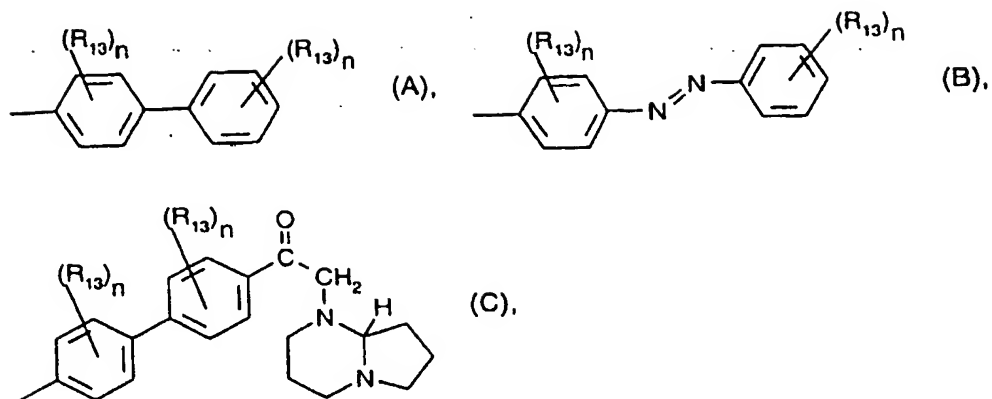
Examples of the  $\text{NR}_8\text{R}_9$  amino group are the respective monoalkyl or dialkylamino groups such as methylamino, ethylamino, propylamino, butylamino, pentylamino, hexylamino, octadecylamino, dimethylamino, diethylamino, dipropylamino, diisopropylamino, di-n-butylamino, di-isobutylamino, dipentylamino, dihexylamino or dioctadecylamino. Further dialkylamino groups are those in which the two radicals independently of one another are branched or unbranched, for example methylethylamino, methyl-n-propylamino, methylisopropylamino, methyl-n-butylamino, methylisobutylamino, ethylisopropylamino, ethyl-n-butylamino, ethylisobutylamino, ethyl-tert-butylamino, isopropyl-n-butylamino or isopropylisobutylamino.

The alkoxy group  $\text{OR}_{10}$  having up to 18 carbon atoms is a branched or unbranched radical such as methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy, octoxy, decyloxy, tetradecyloxy, hexadecyloxy or octadecyloxy. Preference is given to alkoxy having 1 to 12, especially 1 to 8, for example 1 to 6 carbon atoms.

Examples of the thioalkyl group  $\text{SR}_{10}$  are thiomethyl, thioethyl, thiopropyl, thiobutyl, thio-pentyl, thiohexyl, thioheptyl, thiooctyl or thiooctadecyl, it being possible for the alkyl radicals to be linear or branched.

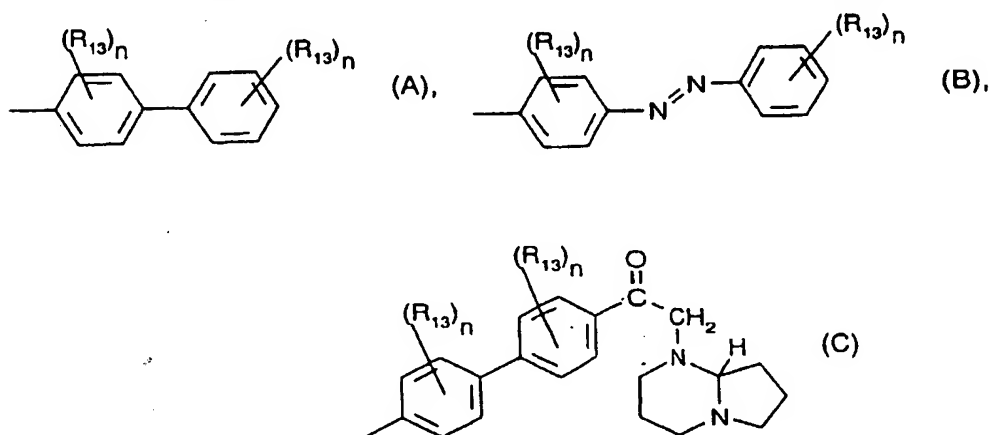
Examples of the radical  $\text{R}_1$  are phenyl, naphthyl, phenanthryl, anthracyl, pyrenyl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thiathrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indoliziny, isoindolyl, indolyl, indazolyl, purinyl, quinoliziny, isoquinolyl, quinolyl, phthalazinyl, naphththyridinyl, quinoxaliny, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl,  $\beta$ -carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazany, biphenyl, stilbenyl, terphenyl, fluorenyl, phenoxazinyl, methoxyphenyl, 2,4-dimethoxyphenyl, 2,4,6-trimethoxyphenyl, bromophenyl, tolyl, xyl, mesityl, nitrophenyl, dimethylaminophenyl, diethylaminophenyl, aminophenyl, diaminophenyl, 1-naphthyl, 2-naphthyl, 1-phenylamino-4-naphthyl, 1-methylnaphthyl, 2-methylnaphthyl, 1-methoxy-2-naphthyl, 2-methoxy-1-naphthyl, 1-dimethylamino-2-naphthyl, 1,2-dimethyl-4-naphthyl, 1,2-dimethyl-6-naphthyl, 1,2-dimethyl-7-naphthyl, 1,3-dimethyl-6-naphthyl, 1,4-dimethyl-6-naphthyl, 1,5-dimethyl-2-naphthyl, 1,6-dimethyl-2-naphthyl, 1-hydroxy-2-naphthyl, 2-hydroxy-1-naphthyl, 1,4-dihydroxy-2-naphthyl, 7-phenanthryl, 1-anthryl, 2-anthryl, 9-anthryl, 3-benzo[b]thienyl,

- 7 -



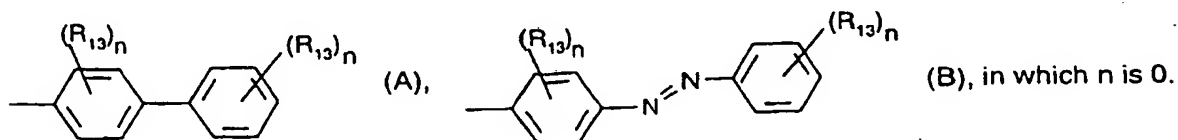
in which  $n$  is 0 and the radicals  $R_8$ ,  $R_9$ ,  $R_{10}$  and  $R_{13}$  are as defined above.

Further particularly preferred compounds are those in which  $R_1$  is phenyl, naphthyl, anthracyl, thioxanthyl, dibenzofuranyl or pyrenyl, the radicals phenyl, naphthyl, anthracyl, thioxanthyl and pyrenyl being unsubstituted or being substituted one or more times by CN,  $NR_8R_9$ ,  $NO_2$ , halogen,  $N_3$ ,  $CF_3$ ,  $SR_{10}$  or  $OR_{10}$ , or  $R_1$  is a radical of the formulae A, B or C.



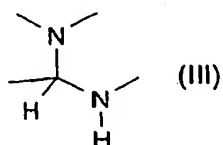
in which  $n$  is 0 and the radicals  $R_8$ ,  $R_9$ ,  $R_{10}$  and  $R_{13}$  are as defined above.

With very particular preference  $R_1$  is phenyl, 4-aminophenyl, 4-methylthiophenyl, 4-trifluoromethylphenyl, 4-nitrophenyl, 2,4,6-trimethoxyphenyl, 2,4-dimethoxyphenyl, naphthyl, anthracyl or pyrenyl or a radical of the formula A or B

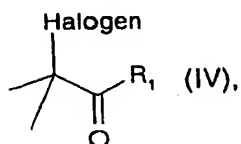


(B), in which  $n$  is 0.

The invention additionally provides a process for preparing compounds having the structural unit of the formula (I), which comprises reacting a compound comprising a structural unit of the formula (III)

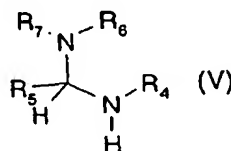


with a compound comprising a structural unit of the formula (IV)

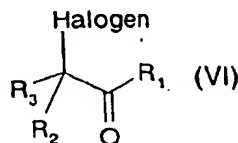


in which R<sub>1</sub> is as defined above, including the preferred meanings, and Halogen is F, Cl, Br or I, preferably Br.

Preference is given to a process for preparing compounds of the formula (II) which comprises reacting a compound of the formula (V)

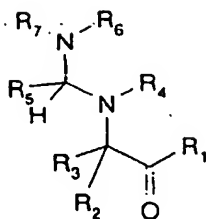


with a compound of the formula (VI)



in which R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> are as defined above, including the preferred meanings, and Halogen is F, Cl, Br or I.

The reaction can be carried out in a conventional manner. It is advantageous to use a solvent or solvent mixture, for example hydrocarbons (benzene, toluene, xylene), halogenated hydrocarbons (methylene chloride, chloroform, carbon tetrachloride, chlorobenzene), alkanols (methanol, ethanol, ethylene glycol monomethyl ether) and ethers (diethyl ether, dibutyl ether, ethylene glycol dimethyl ether) or mixtures thereof.



in which the radicals  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$  are as defined above,

including their preferred meanings.

The base-catalysed addition or substitution reaction can be carried out with low molecular mass compounds (monomers), with oligomers, with polymeric compounds or with a mixture of these compounds. Examples of reactions which can be carried out both with monomers and with oligomers/polymers using the novel photoinitiators are the Knoevenagel reaction or the Michael addition reaction.

Of particular importance are compositions in which component B) is an anionically polymerizable or crosslinkable organic material.

The organic material can be in the form of mono- or polyfunctional monomers, oligomers or polymers.

Particularly preferred oligomeric/polymeric systems are binders or coating systems as are customary in the coatings industry.

Examples of such base-catalysable binders or coating systems are:

- a) Acrylate copolymers having alkoxysilane or alkoxysiloxane side groups, for example the polymers described in US-A-4,772,672 or US-A-4,444,974;
- b) Two-component systems comprising hydroxyl-containing polyacrylates, polyesters and/or polyethers and aliphatic or aromatic polyisocyanates;
- c) Two-component systems comprising functional polyacrylates and a polyepoxide, where the polyacrylate contains carboxyl or anhydride groups;
- d) Two-component systems comprising fluorine-modified or silicone-modified hydroxyl-containing polyacrylates, polyesters and/or polyethers and aliphatic or aromatic polyisocyanates;
- e) Two-component systems comprising (poly)ketimines and aliphatic or aromatic polyisocyanates;

enically unsaturated carbonyl compound employed can be any double bond activated by a carbonyl group. Examples are esters or amides of acrylic acid or methacrylic acid. In the ester groups it is also possible for additional hydroxyl groups to be present. Diesters and triesters are also possible.

Typical examples are hexanediol diacrylate or trimethylolpropane triacrylate. Instead of the acrylic acid it is also possible to use other acids and their esters or amides, such as crotonic or cinnamic acid.

Under base catalysis, the components of the system react with one another at room temperature to form a crosslinked coating system which is suitable for numerous applications. Owing to its good inherent weathering resistance it is suitable, for example, for exterior applications as well and can, if required, be additionally stabilized by UV absorbers and other light stabilizers.

Other systems suitable as component B) in the novel compositions are epoxy systems. Epoxy resins are suitable for preparing novel, curable mixtures comprising epoxy resins as component B) are those which are customary in epoxy resin technology, examples of such epoxy resins being:

- I) Polyglycidyl and poly( $\beta$ -methylglycidyl) esters, obtainable by reacting a compound, having at least two carboxyl groups in the molecule with epichlorohydrin or  $\beta$ -methyl-epichlorohydrin. The reaction is judiciously carried out in the presence of bases. As the compound having at least two carboxyl groups in the molecule it is possible to use aliphatic polycarboxylic acids. Examples of such polycarboxylic acids are oxalic, succinic, glutaric, adipic, pimelic, suberic, azelaic or dimerized or trimerized linoleic acid. It is also possible, however, to employ cycloaliphatic polycarboxylic acids, such as tetrahydrophthalic, 4-methyltetrahydrophthalic, hexahydrophthalic or 4-methylhexahydrophthalic acid, for example. Aromatic polycarboxylic acids, furthermore, can be used, such as phthalic, isophthalic or terephthalic acid, for example.
- II) Polyglycidyl or poly( $\beta$ -methylglycidyl) ethers, obtainable by reacting a compound having at least two free alcoholic hydroxyl groups and/or phenolic hydroxyl groups with epichlorohydrin or  $\beta$ -methyl-epichlorohydrin under alkaline conditions or in the presence of an acidic catalyst with subsequent alkali treatment.

The glycidyl ethers of this type are derived, for example, from acyclic alcohols, such as ethylene glycol, diethylene glycol and higher poly(oxyethylene) glycols, propane-1,2-diol or



The compositions comprise the photoinitiator, component A), preferably in an amount of from 0.01 to 10% by weight, based on the component B).

In addition to the photoinitiator, component A), the photopolymerizable mixtures may include various additives. Examples of these are thermal inhibitors which are intended to prevent premature polymerization, such as hydroquinone, hydroquinone derivatives, p-methoxyphenol,  $\beta$ -naphthol or sterically hindered phenols such as 2,6-di(tert-butyl)-p-cresol, for example. To increase the dark storage stability it is possible, for example, to use copper compounds, such as copper naphthenate, stearate or octoate, phosphorus compounds, such as triphenylphosphine, tributylphosphine, triethyl phosphite, triphenyl phosphite or tribenzyl phosphite, quaternary ammonium compounds, such as tetramethylammonium chloride or trimethylbenzylammonium chloride, or hydroxylamine derivatives, such as N-diethyl-hydroxylamine. To exclude atmospheric oxygen during polymerization it is possible to add paraffin or similar waxlike substances, which owing to their lack of solubility in the polymer migrate to the surface at the beginning of polymerization where they form a transparent surface layer which prevents the ingress of air. It is likewise possible to apply an oxygen-impermeable layer. Light stabilizers which can be added, in a small amount, are UV absorbers such as those, for example, of the hydroxyphenylbenzotriazole, hydroxyphenyl-benzophenone, oxalamide or hydroxyphenyl-s-triazine type. Individual compounds or mixtures of these compounds can be used, with or without the deployment of sterically hindered amines (HALS).

Examples of such UV absorbers and light stabilizers are given below.

1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octoxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis( $\alpha,\alpha$ -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-

n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione.

6. Oxalamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyloxanilide, 2,2'-di-dodecyloxy-5,5'-di-tert-butyloxanilide, 2-ethoxy-2'-ethyl oxanilide, N,N'-bis(3-dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyloxanilide, mixtures of o- and p-methoxy- and of o- and p-ethoxy-disubstituted oxanilides.

7. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-dodecyl/tridecyloxy-(2-hydroxypropyl)oxy-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

8. Phosphites and phosphonites, for example, triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, bis-isodecyloxy pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tri-tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylenediphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyldibenzo[d,g]-1,3,2-dioxaphosphocin, bis-(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite.

Examples of further additives are:

Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass beads, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibres of other natural products, synthetic fibres.

or tetraacrylate, vinyl acrylate, divinyl benzene, divinyl succinate, diallyl phthalate, triallyl phosphate, triallyl isocyanurate or tris(2-acryloylethyl)isocyanurate.

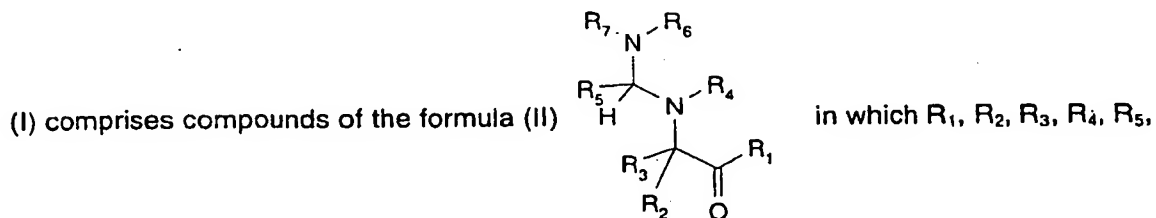
Examples of polyunsaturated compounds of relatively high molecular mass (oligomers) are acrylicized epoxy resins, acrylicized polyesters or polyesters containing vinyl ether groups or epoxy groups, polyurethanes and polyethers. Further examples of unsaturated oligomers are unsaturated polyester resins which are mostly prepared from maleic acid, phthalic acid and one or more diols and have molecular weights of from about 500 to 3000. In addition it is also possible to employ vinyl ether monomers and oligomers, and also maleate-terminated oligomers with polyester, polyurethane, polyether, polyvinyl ether and epoxy main chains. In particular, combinations of vinyl ether-functional oligomers and polymers as are described in WO 90/01512 are very suitable. Also suitable, however, are copolymers of vinyl ether and maleic acid-functionalized monomers. Unsaturated oligomers of this kind can also be referred to as prepolymers.

Particularly suitable examples are esters of ethylenically unsaturated carboxylic acids and polyols or polyepoxides, and polymers having ethylenically unsaturated groups in the chain or in side groups, such as unsaturated polyesters, polyamides and polyurethanes and copolymers thereof, alkyd resins, polybutadiene and butadiene copolymers, polyisoprene and isoprene copolymers, polymers and copolymers having (meth)acrylic groups in side chains, and mixtures of one or more such polymers.

If, in addition, use is made of such free-radically curable monomers, oligomers/polymers then it is judicious to add a further photoinitiator which dissociates into free radicals. Such photoinitiators are known and are produced industrially. Examples are benzophenone, benzophenone derivatives, acetophenone, acetophenone derivatives, for example  $\alpha$ -hydroxycycloalkyl phenyl ketones, dialkoxyacetophenones,  $\alpha$ -hydroxy- or  $\alpha$ -aminoacetophenones, 4-aryl-1,3-dioxolanes, benzoin alkyl ethers and benzil ketals, monoacyl phosphine oxides, bisacylphosphine oxides, ferrocenium compounds or titanocenes.

Examples are specified in US Patent 5077402. Polymer systems of this kind, in which curing/crosslinking takes place by different mechanisms, are also referred to as hybrid systems.

Component A) is preferably an organic compound in which the structural unit of the formula



R<sub>6</sub> and R<sub>7</sub> are as defined above, including their preferred meanings.

Examples and preferred meanings for base-catalysed reactions have already been given above.

With particular preference, component B) is an anionically polymerizable or crosslinkable organic material.

In some cases it may be advantageous to carry out heating during or after exposure to light. In this way it is possible in many cases to accelerate the crosslinking reaction.

The sensitivity of the novel compositions to light generally extends from about 200 nm through the UV region and into the infrared region (about 20,000 nm, in particular 1200 nm) and therefore spans a very broad range. Suitable radiation comprises, for example, sunlight or light from artificial light sources. Therefore, a large number of very different types of light source can be used. Both point sources and flat radiators (lamp carpets) are suitable. Examples are carbon arc lamps, xenon arc lamps, medium-pressure, high-pressure and low-pressure mercury lamps, doped if desired with metal halides (metal halogen lamps), microwave-stimulated metal vapour lamps, excimer lamps, superactinic fluorescent tubes, fluorescent lamps, incandescent argon lamps, electronic flashlights, photographic flood lamps, electron beams and X-rays, produced by means of synchrotrons or laser plasma. The distance between the lamp and the substrate according to the invention which is to be exposed can vary depending on the application and on the type and/or power of the lamp, for example between 2 cm and 150 cm. Also especially suitable are laser light sources, for example excimer lasers. Lasers in the visible region or in the IR region can also be employed. Very advantageous here is the high sensitivity of the novel materials and the possibility of adapting a dye as coinitiator to the laser line. By this method it is possible to

form of films, and also metals such as Al, Cu, Ni, Fe, Zn, Mg or Co and GaAs, Si or SiO<sub>2</sub>, on which it is the intention to apply a protective coating or, by imagewise exposure, an image.

The substrates can be coated by applying a liquid composition, a solution or suspension to the substrate. The choice of solvent and the concentration depend predominantly on the type of composition and the coating process. The solvent should be inert: in other words, it should not undergo any chemical reaction with the components and should be capable of being removed again after the coating operation, in the drying process. Examples of suitable solvents are ketones, ethers and esters, such as methyl ethyl ketone, isobutyl methyl ketone, cyclopentanone, cyclohexanone, N-methylpyrrolidone, dioxane, tetrahydrofuran, 2-methoxyethanol, 2-ethoxyethanol, 1-methoxy-2-propanol, 1,2-dimethoxyethane, ethyl acetate, n-butyl acetate and ethyl 3-ethoxypropionate.

Using known coating processes, the solution is applied uniformly to a substrate, for example by spin coating, dip coating, knife coating, curtain coating, brushing, spraying - especially electrostatic spraying - and reverse roll coating and by electrophoretic deposition. It is also possible to apply the photosensitive layer to a temporary, flexible support and then to coat the final substrate, for example a copper-clad circuit board, by means of layer transfer via lamination.

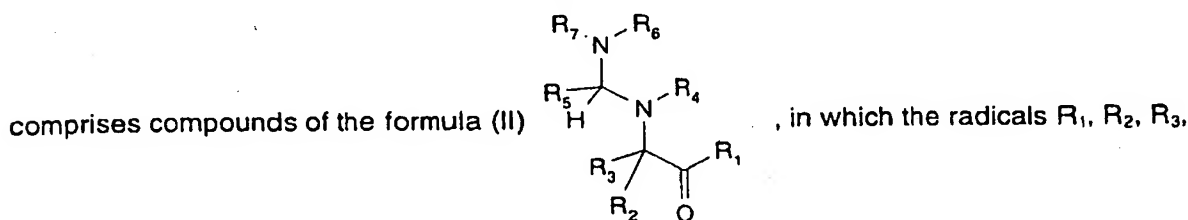
The amount applied (layer thickness) and the nature of the substrate (layer support) are functions of the desired field of application. The range of layer thicknesses generally comprises values from about 0.1  $\mu\text{m}$  to more than 100  $\mu\text{m}$ .

The novel radiation-sensitive compositions can also be subjected to imagewise exposure. In this case they are used as negative resists. They are suitable for electronics (galvanoresists, etch resists and solder resists), for the production of printing plates, such as offset printing plates, flexographic and relief printing plates or screen printing plates, for the production of marking stamps, and can be used for chemical milling or as micro resists in the production of integrated circuits. There is a correspondingly wide range of variation in the possible layer supports and in the processing conditions of the coated substrates.

The term "imagewise" exposure relates both to exposure through a photomask containing a predetermined pattern, for example a slide, exposure by a laser beam which is moved under

heteroaromatic radical which is capable of absorbing light in the wavelength range from 200 to 650 nm and on doing so brings about cleavage of the adjacent carbon-nitrogen bond, as a photoinitiator for photochemically induced, base-catalysed addition or substitution reactions.

Preference is given to an organic compound in which the structural unit of the formula (I)



R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> are as defined above, including their preferred meanings.

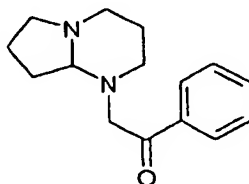
Examples and preferences for base-catalysed addition or substitution reactions have been given above.


The invention provides, furthermore, a coated substrate which has been coated on at least one surface with a composition as described above, and a process for the photographic production of relief images, in which a coated substrate is subjected to imagewise exposure and then the unexposed areas are removed with a solvent. Of particular interest in this context is the abovementioned exposure by means of a laser beam.

The examples which follow illustrate the invention. As in the remainder of the description and in the claims, parts and percentages are by weight unless stated otherwise. If alkyl or alkoxy radicals having more than three C atoms are indicated without reference to their isomeric form, then the respective n-isomers are meant.

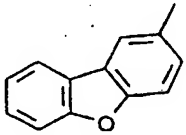
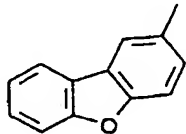
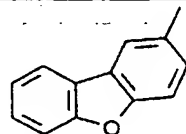
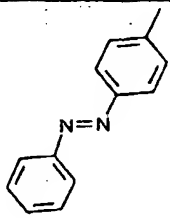
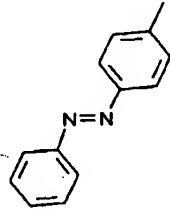
#### A-Examples: Preparing the photoinitiators

##### Example A1



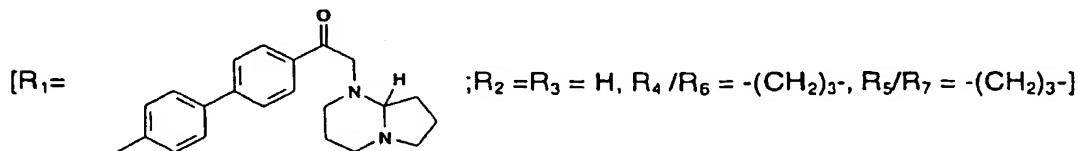


### Example A5

Example	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>5</sub> /R <sub>7</sub>	R <sub>4</sub> /R <sub>6</sub>
A21	4-Trifluoromethylphenyl	H	H	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A22	4-Dimethylaminophenyl	H	H	-(CH <sub>2</sub> ) <sub>3</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A23	4-Dimethylaminophenyl	H	H	-(CH <sub>2</sub> ) <sub>3</sub> -NH-	-(CH <sub>2</sub> ) <sub>3</sub> -
A24	4-Dimethylaminophenyl	H	H	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A25	2,4,6-Trimethoxyphenyl	H	H	-(CH <sub>2</sub> ) <sub>3</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A26	2,4,6-Trimethoxyphenyl	H	H	-(CH <sub>2</sub> ) <sub>3</sub> -NH-	-(CH <sub>2</sub> ) <sub>3</sub> -
A27	2,4,6-Trimethoxyphenyl	H	H	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A28	4-(C <sub>14</sub> H <sub>29</sub> -O)phenyl	H	H	-(CH <sub>2</sub> ) <sub>3</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A29	4-(C <sub>14</sub> H <sub>29</sub> -O)phenyl	H	H	-(CH <sub>2</sub> ) <sub>3</sub> -NH-	-(CH <sub>2</sub> ) <sub>3</sub> -
A30	4-(C <sub>14</sub> H <sub>29</sub> -O)phenyl	H	H	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A31		H	H	-(CH <sub>2</sub> ) <sub>3</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A32		H	H	-(CH <sub>2</sub> ) <sub>3</sub> -NH-	-(CH <sub>2</sub> ) <sub>3</sub> -
A33		H	H	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A34		H	H	-(CH <sub>2</sub> ) <sub>3</sub> -	-(CH <sub>2</sub> ) <sub>3</sub> -
A35		H	H	-(CH <sub>2</sub> ) <sub>3</sub> -NH-	-(CH <sub>2</sub> ) <sub>3</sub> -



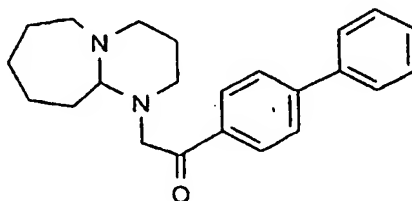
Example	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>
A40	Phenyl	H	H	H	NH <sub>2</sub>	H	H
A41	Phenyl	H	H	H	NH(C <sub>2</sub> H <sub>5</sub> )	C <sub>2</sub> H <sub>5</sub>	H
A42	Phenyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	H	H
A43	Phenyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	H	CH <sub>3</sub>
A44	Phenyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	H	H
A45	Phenyl	H	H	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>
A46	Phenyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>
A47	Phenyl	H	H	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	H	CH <sub>3</sub>
A48	Phenyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	H	CH <sub>3</sub>
A49	Phenyl	H	H	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	H	CH <sub>3</sub>
A50	Naphthyl	H	H	H	NH <sub>2</sub>	H	H
A51	Naphthyl	H	H	H	NH(C <sub>2</sub> H <sub>5</sub> )	C <sub>2</sub> H <sub>5</sub>	H
A52	Naphthyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	H	H
A53	Naphthyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	H	CH <sub>3</sub>
A54	Naphthyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	H	H
A55	Naphthyl	H	H	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>
A56	Naphthyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>
A57	Naphthyl	H	H	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	H	CH <sub>3</sub>
A58	Naphthyl	H	H	H	N(CH <sub>3</sub> ) <sub>2</sub>	H	CH <sub>3</sub>
A59	Naphthyl	H	H	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	H	CH <sub>3</sub>

Example A 60

U.V. (CHCl<sub>3</sub>) max. at 245 nm ( $\epsilon$  6700) and 330 nm ( $\epsilon$  23100).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) [ppm]: 8.20 (2H, d, ArH), 7.89-7.43 (7H, m, ArH), 4.03 (1H, d, NCH<sub>2</sub>CO), 3.49 (1H, d, NCH<sub>2</sub>CO), 3.05 (2H, m, NCH<sub>2</sub>), 2.91 (1H, m, NCH), 2.60 (1H, m, NCH) and 2.3-1.4 (8H, m, CH<sub>2</sub>).

Example A63:



Orange-colored oil (yield 78%)

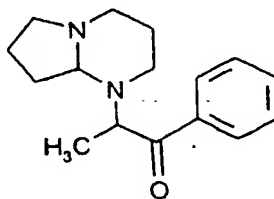
U.V. (CHCl<sub>3</sub>) max. at 287 nm ( $\epsilon$  20500).

I.R. (KBr) 1690 cm<sup>-1</sup> (C=O).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>) [ppm]: 1989.14, 145.64, 139.79, 134.85, 128.97, 128.82, 128.22, 127.29, 127.16, 125.33, 82.15, 56.34, 55.51, 53.57, 52.10, 32.90, 29.07, 24.42, 24.61 and 21.48.

Example A64:

[R<sub>1</sub> = phenyl, R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = H, R<sub>4</sub>/R<sub>6</sub> = -(CH<sub>2</sub>)<sub>3</sub>-, R<sub>5</sub>/R<sub>7</sub> = -(CH<sub>2</sub>)<sub>3</sub>-]



Orange-coloured oil (yield 86%)

I.R. (KBr) 1695 cm<sup>-1</sup> (C=O).

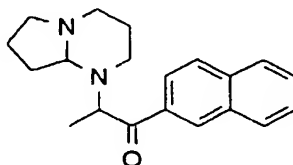
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) [ppm]: 8.17 (2H, d, J=7.0 Hz, ArH), 7.50-7.35 (3H, m, ArH), 4.50 (1H, q, J = 6.6 Hz, NHCHCH<sub>3</sub>), 3.05 (2H, m, NCH<sub>2</sub>), 2.69 (2H, m, NCH<sub>2</sub>), 2.49 (1H, m, NCH), 2.3-1.3 (8H, m, CH<sub>3</sub>) and 1.16 (3H, d, J= 6.6 Hz, CH<sub>3</sub>).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>) [ppm]: 200.72, 136.61, 132.65, 129.31, 128.37, 81.83, 60.09, 52.31, 51.40, 45.50, 28.76, 25.01, 19.21 and 6.55.

\* The compound of Example 76 is obtained as follows: a base-catalysed coupling reaction of thiosalicylic acid and p-bromacetophenone in the presence of copper is used to obtain the keto acid which, following dehydrogenation with polyphosphoric acid, gives the 2-acetylthioxanthone, which is brominated in the  $\alpha$  position. Finally, the reaction of the ketone with 1,5-diazabicyclo[4.3.0]nonane gives the compound A76.

#### Example A83

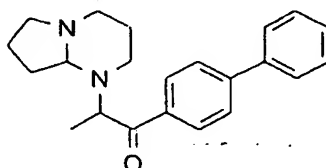
[R<sub>1</sub> = 2-naphthyl, R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = H, R<sub>4</sub>/R<sub>6</sub> = -(CH<sub>2</sub>)<sub>3</sub>-, R<sub>5</sub>/R<sub>7</sub> = -(CH<sub>2</sub>)<sub>3</sub>-]



<sup>1</sup>H NMR (CDCl<sub>3</sub>) [ppm]: 8.85 (0.65H, s), 8.68 (0.35H, s), 8.44-7.44 (6H, m, ArH), 4.63 (0.65H, q, J 6.5 Hz, NCHCH<sub>3</sub>), 4.61 (0.35H, q, J 6.9Hz, NCHCH<sub>3</sub>), 3.14-2.53 (4H, m), 2.28-1.38 (9H, m), 1.39 (1.05H, d, J 6.9Hz, CH<sub>3</sub>) and 1.22 (1.95H, d, J 6.5Hz, CH<sub>3</sub>).

#### Example A84

[R<sub>1</sub> = diphenyl, R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = H, R<sub>4</sub>/R<sub>6</sub> = -(CH<sub>2</sub>)<sub>3</sub>-, R<sub>5</sub>/R<sub>7</sub> = -(CH<sub>2</sub>)<sub>3</sub>-]



<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.25 (1.5H, m, ArH), 8.01 (0.5H, m, ArH), 7.60 (3H, m, ArH), 7.40 (4H, m, ArH), 4.53 (0.75H, q, J 6.6 Hz, NCHCH<sub>3</sub>), 4.45 (0.25H, q, J 7.0 Hz, NCHCH<sub>3</sub>), 3.08 (2H, m), 2.73-1.46 (11H, m), 1.36 (0.75H, d, J 7.0 Hz, CH<sub>3</sub>), 1.19 (2.25H, d, J 6.5 Hz, CH<sub>3</sub>).

**B-Examples: Use: Base catalysis with monomeric compounds**

Examples B1-B4 UV-initiated Michael addition.

7.4 · 10<sup>-5</sup> mol of photoinitiator (latent amidine base) are dissolved in a mixture of dimethyl malonate and n-butyl acrylate (1:1, 200 mg corresponding to 7.4 · 10<sup>-4</sup> mol) in a quartz vessel. The mixture is irradiated with a high-pressure mercury lamp (200 W) from a distance of 30 cm. The conversion is monitored as a function of time.

**C-Examples: Use: Base catalysis with oligomeric/polymeric compounds****Examples C1-C6**

Preparation of a urethane acrylate based on isophorone diisocyanate and 4-hydroxybutyl acrylate.

The reaction is carried out under a nitrogen atmosphere and all commercial chemicals used are employed without further purification.

1566.8 g (13.78 mol of NCO) of isophorone diisocyanate, 2.3 g of dibutyltin dilaurate, 2.3 g of 2,5-di-*t*-butyl-*p*-cresol and 802.8 g of butyl acetate are charged to a three-necked flask with condenser and dropping device. Dry nitrogen is bubbled through the reaction mixture and the temperature is slowly raised to 60°C. 1987 g (13.78 mol) of 4-hydroxybutyl acrylate are added, during which the reaction solution warms slowly to 80°C. The temperature is held at 80°C and the dropping device is flushed with butyl acetate (86.6 g). The reaction is monitored by titration of the remaining amount of isocyanate, and is over when the isocyanate content is below 0.2% based on the solids content. The reaction product obtained has the following physical properties:

Residual 4-hydroxybutyl acrylate: < 0.002% based on solids (HPLC analysis),

Colour: << Gardner 1,

Viscosity: 43 cPa s (20°C),

Solids content: 79,3% (1 hour at 140°C),

GPC data (polystyrene standard):  $M_n$  778,  $M_w$  796,  $d=1.02$ .

**Preparation of a malonate polyester**

The reaction is carried out under a nitrogen atmosphere and all commercial chemicals used are employed without further purification.

In a reaction vessel with stirrer and condenser 1045 g of 1,5-pentanediol, 1377.4 g of diethyl malonate and 242.1 g of xylene are carefully refluxed. The maximum temperature of the reaction mixture is 196°C while the temperature at the head of the condenser is held at 79°C. In this way 862 g of ethanol, corresponding to a conversion of 97.7%, are distilled off. Then xylene is stripped off in vacuo at a temperature of 200°C. The resulting polymer has a solids content of 98.6%, a viscosity of 2710 mPa s and an acid number of 0.3 mg of KOH/g based on the solids content.  $M_n$  is 1838,  $M_w$  is 3186, the colour is 175 on the APHA (American Public Health Association) scale (Hazen colour number; ISO 6271).

Example C6 Curing with visible light

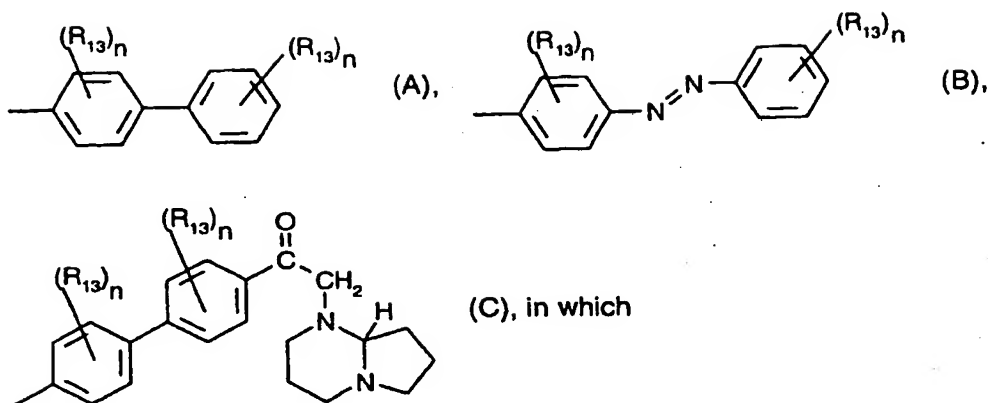
18.8 mg ( $6.4 \times 10^{-5}$  mol) of the photoinitiator from Example A1 and 10 mg of isopropyl-9H-thioxanthone ( $6.4 \times 10^{-5}$  mol) are dissolved in 400 mg of a 1.3:1 mixture of the above-described urethane acrylate and the malonate polyester. A film 50  $\mu\text{m}$  thick is drawn out onto a glass plate and is exposed using a halogen lamp (500 W) at a distance of 30 cm. The polymer film is tack-free after 120 minutes.

Examples C7-C8

The amounts of photoinitiator from Example A3 and isopropyl-9H-thioxanthone (ITX) stated in Table 6 are dissolved in 400 mg of a 1.3:1 mixture of the above-described urethane acrylate and the malonate polyester. A film 50  $\mu\text{m}$  thick is drawn out onto a glass plate and is exposed using a TL03/40 W lamp at a distance of 30 cm. After 4, 6 and 24 hours the König pendulum hardness (DIN 53157) and the Yellowness Index in accordance with ASTM D 1925-88 are determined in each case. The results are reproduced in Table 7.

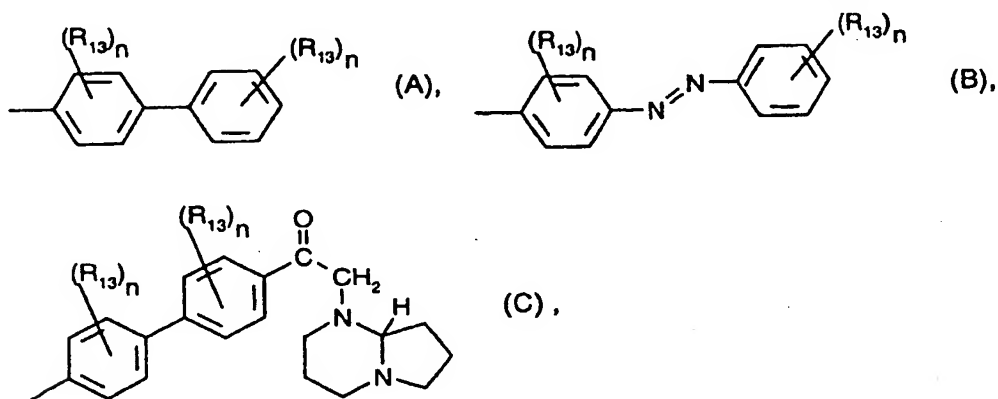
Table 7

Example	Initiator	Pendulum hardness		
		4 h	6 h	24 h
C7	25.0 parts of A3 12.5 parts of ITX	48	71	154
C8	25.0 parts of A3 5.0 parts of ITX	52	92	130



$R_{13}$  is  $C_1$ - $C_{18}$ alkyl,  $C_2$ - $C_{18}$ alkenyl,  $C_2$ - $C_{18}$ alkynyl,  $C_1$ - $C_{18}$ haloalkyl,  $NO_2$ ,  $NR_8R_9$ ,  $OH$ ,  $CN$ ,  $OR_{10}$ ,  $SR_{10}$ ,  $C(O)R_{11}$ ,  $C(O)OR_{12}$  or halogen;  
 $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  are hydrogen or  $C_1$ - $C_{18}$ alkyl; and  
 $n$  is 0 or a number 1, 2 or 3.

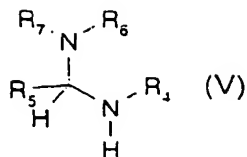
3. An organic compound according to claim 1, wherein  $R_1$  is phenyl, naphthyl, anthracyl, thioxanthyl, dibenzofuryl or pyrenyl, the radicals phenyl, naphthyl, anthracyl, thioxanthyl and pyrenyl being unsubstituted or being substituted one or more times by  $CN$ ,  $N_3$ ,  $NR_8R_9$ , halogen,  $NO_2$ ,  $CF_3$ ,  $SR_{10}$  or  $OR_{10}$ , or  $R_1$  is a radical of the formulae A, B or C



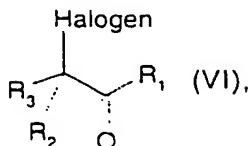
in which  $n$  is 0 and the radicals  $R_8$ ,  $R_9$ ,  $R_{10}$  and  $R_{13}$  are as defined in claim 2.

4. An organic compound according to claim 1, wherein  $R_2$  and  $R_3$  independently of one another are hydrogen,  $C_1$ - $C_6$ alkyl or phenyl.



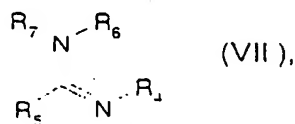


with a compound of the formula VI



in which  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$  are as defined in claim 1 and Halogen is F, Cl, Br or I.

9. A process for preparing a compound of the formula VII,



wherein  $R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$  are as defined in claim 1,

which process comprises exposing a compound of the formula II according to claim 1 to light having a wavelength from 200 nm to 650 nm.

10. A composition comprising

- A) at least one compound of the formula II according to claim 1 and
- B) at least one organic material capable of a base-catalysed addition or substitution reaction.

11. A composition according to claim 10, wherein component B) is an anionically polymerizable or crosslinkable organic material.

12. A composition according to claim 10, wherein component B) is one of the following systems:

- b) a two-component system comprising hydroxyl-containing polyacrylates, polyesters and/or polyethers and aliphatic or aromatic polyisocyanates;
- c) a two-component system comprising functional polyacrylates and a polyepoxide, where the polyacrylate contains carboxyl or anhydride groups;



- 47 -

21. Organic compounds of the formula (II), processes for preparing same, or  
compositions or uses involving/containing same, substantially as hereinbefore  
5 described with reference to the Examples.

DATED this 29th day of February, 2000

**CIBA SPECIALTY CHEMICALS HOLDING INC**

10 By its Patent Attorneys

**DAVIES COLLISON CAVE**

15

20

25

